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Short communication

Evaluation of a new electrochemical concept for vacuum toilet wastewater treatment – Comparison with ozonation and peroxone processes

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ABSTRACT

New electrochemical advanced oxidation processes (EAOPs) are becoming increasingly attractive for use in wastewater treatment. A reactor with a boron-doped diamond anode and a gas diffusion cathode seems to be a promising approach for water purification, because of the in situ generation of highly reactive species such as anodic $^{\bullet}OH$ radicals and cathodic H_2O_2.

To evaluate the application potential of this EAOP concept, the treatment efficiency and energy efficiency were compared with those of well-established AOPs such as ozonation and peroxone processes (O_3 + H_2O_2). In this study, the innovative electrochemical batch treatment of artificial toilet wastewater showed a COD degradation efficiency of 38.1%, which is higher than that obtained using ozonation (17.0%) or the peroxone process (25.7%). Additionally, the specific energy demand is lower for EAOP (93.6 kWh/kg m_{COD}) than for ozonation (125.4 kWh/kg m_{COD}) or the peroxone process (134.5 kWh/kg m_{COD}).

1. Introduction

Over the last several years, the removal of more than 160 micropollutants from wastewater has been investigated [1]. Fortunately, some pharmaceuticals are easily degraded in conventional municipal wastewater treatment plants (WWTP), but many of them are persistent and pass through the WWTP without sufficient degradation. According to the literature, the removal efficiencies of two standard analgesics, acetaminophen and diclofenac, are approx. 99% and 30%, respectively [2,3]. This can lead to contamination of downstream bodies of water. In view of the fact that water is a valuable asset that should be protected, it is necessary to increase efforts to remove persistent pharmaceuticals. Therefore, additional treatment is often necessary.

Options for such additional treatment include activated carbon adsorption [4], nanofiltration [5] and advanced oxidation processes (AOPs) [6]. One of the most (cost) efficient AOPs is ozonation [7], which proceeds by two pathways: (a) direct reaction and (b) $^{\bullet}OH$ reaction [8]. Ozone still has a high oxidation potential (2.07 V), even higher than those of chlorine (1.36 V) and H_2O_2 (1.77 V) [9]. Ozonation is already implemented in some WWTPs in Europe [10]. However, ozonation is not able to adequately remove all residues, e.g. X-ray contrast media [11]. For this purpose, electrochemical oxidation processes (EAOPs) based on boron-doped diamond electrodes (BDDs) are much more effective [12]. By applying electrical energy to BDDs, it is possible to generate highly reactive species, especially $^{\bullet}OH$, in situ, at a much higher concentration than in ozone processes [13].

It should be borne in mind that EAOPs are still an emerging technology, especially for water reuse applications, and might even produce toxic intermediates [14,15]. One of the biggest disadvantages is the relatively high operational costs due to the electrical energy demand. Electrochemical reactors based on two BDDs are especially cost-intensive [16], particularly in comparison to ozonation or peroxone (O_3 plus H_2O_2) processes. With the prevailing energy transition from fossil to renewable energies EAOPs are becoming more sustainable, but the cost of electrical power is still a limiting factor [17].

For these reasons, an engineering-approved electrochemical reactor concept was investigated, based on one BDD (anode) with a gas diffusion electrode (GDE) as the cathode. This innovative reactor concept combines the simultaneous generation of highly reactive $^{\bullet}OH$ on the BDD surface and H_2O_2 on the GDE surface, which should be very energy efficient as there is double use of the applied power [13,18]. Striving for even more cost savings, the reactor system is membraneless to shift the ohmic drop to a minimum. Such a configuration is only possible with the selected GDEs, because conventional dimensionally stable cathodes generate hydrogen which would result in a high risk of oxyhydrogen gas explosion due to the possible formation of oxygen and chlorine at the anode [15].

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Table 1
Components and concentrations of artificial wastewater.

Chemicals	Concentration [g/L]
Urea	23.8
Sodium sulfate decahydrate	6.6
Sodium dihydrogen phosphate dihydrate	6.4
Magnesium sulfate heptahydrate	0.6
Calcium chloride dihydrate	0.6
Glucose	4.0
Tryptone	0.3
Meat extract	0.3

2. Experimental

2.1. Composition of the artificial wastewater

In this study, the same formulation of wastewater (WW) was subjected to ozonation, a peroxone process and BDD/GDE treatment. To ensure reproducibility, an artificial solid-free WW was used (see Table 1). The components and concentration of the artificial WW represents WW from train vacuum toilets and was previously developed in cooperation with train toilet operators. A solid-free WW was chosen, as a future concept for integration in trains includes a pretreatment step (e.g. sedimentation, filtration) to prevent clogging caused by solids.

2.2. Ozone and peroxone reactor setup

The experimental setup for ozonation (see Fig. 1) is composed of an O_3 generator (Anseros Generator COM, Germany), a reactor, an O_3 concentration measurement device (Anseros Ozomat GM, Germany) and an O_3 destroyer to eliminate the unreacted O_3 (Fig. 2). Experiments were conducted using different O_3 gas flow rates: 31, 51, 66 and 81 mg/L O_3.

The generated O_3 is led directly through a bubble diffuser (Dae Yang, ∅ 13 cm, China) at the bottom of a reactor filled with 2 L WW in each experiment. A magnetic stirrer was placed on top of the bubble diffuser to disperse the O_3 bubbles. About 2 cm above the bubble diffuser a basket made of a PTFE mesh was mounted to provide a glass packing (cylinders, 3 mm diameter). This basket works as a packed-bed reactor, which promises an enhancement of energy yield [19]. A hose pump (Behr PLP 330, Germany) was connected to the reactor for COD sampling.

The difference between O_3 input and output is the net volume of the gas which reacted with the artificial WW and which is the relevant value for further calculations:

$$m_{O_3,net} = \int (\dot{V}_{in} \cdot c_{O_3,in} - \dot{V}_{out} \cdot c_{O_3,out}) dt \quad (1)$$

The same experimental setup was used for the peroxone process. The O_3 gas flow was kept at 81 mg/L. Furthermore, every 30 min 2 mL of H_2O_2 (30 wt% solution) was added into the reactor, forming radicals according to the following equations [20]:

$$H_2O_2 \leftrightharpoons HO_2^- + H^+ \quad (2)$$

$$HO_2^- + O_3 \rightarrow HO_2^\bullet + O_3^- \quad (3)$$

2.3. Electrolysis cell setup

The two main components of the undivided electrolysis cell are the anodic BDD (Condias, Germany) and the cathodic GDE (Covestro, Germany). A frame was mounted between the electrodes to provide a defined gap (6.5 mm). The WW was pumped upwards from the tank (1 L volume) with a constant flow rate of 280 mL/min using a hose pump (Behr PLP 330, Germany) through the cell. The active area of each electrode is 25 cm^2. All parts were sealed with silicon and tightened in a housing. The gas side of the GDE was open to the atmosphere for oxygen diffusion (Fig. 3).

The power was applied using a DC-Adapter (Conrad PS-303D, Germany), voltage and current were plotted with multimeters (Voltcraft VC220, Germany). The temperature was monitored by a PT100 thermometer (Voltcraft K202, Germany). All experiments were conducted with a current of 3 A.

2.4. Analytical methods

The chemical oxygen demand (COD) was determined photometrically using quick tests (Macherey-Nagel CSB 1500, Germany). It should be noted that H_2O_2 negatively affects the COD determination via quick tests and the actual value is lower than the measured value. For that reason, the additional H_2O_2 was destroyed by heating the sample to approx. 50 °C.

3. Results and discussion

3.1. Ozonation and peroxone processes

Table 2 shows the results of the ozonation process, in which the artificial WW was treated with different O_3 inputs, and H_2O_2 was added for the peroxone process. All experiments were conducted in the same O_3 reactor with a reaction time of 4 h. The COD_{start} value differed slightly between runs, as the artificial WW was freshly mixed for each experiment to avoid aging and due to statistical errors during the COD determination.

As expected, increasing the O_3 input leads to a higher COD removal, as there is more O_3 to react with the artificial WW. The COD removal during the experiment with 81 mg/L O_3 is about five times higher than in the experiment with 31 mg/L (run 4), although the O_3 concentration

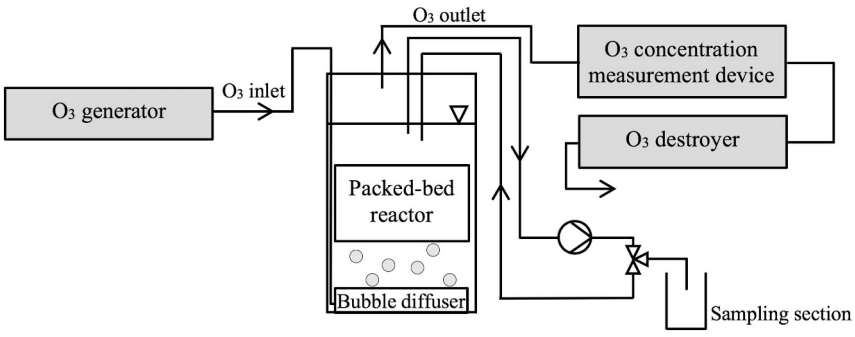

Fig. 1. Schematic diagram of the experimental setup of the ozone reactor.

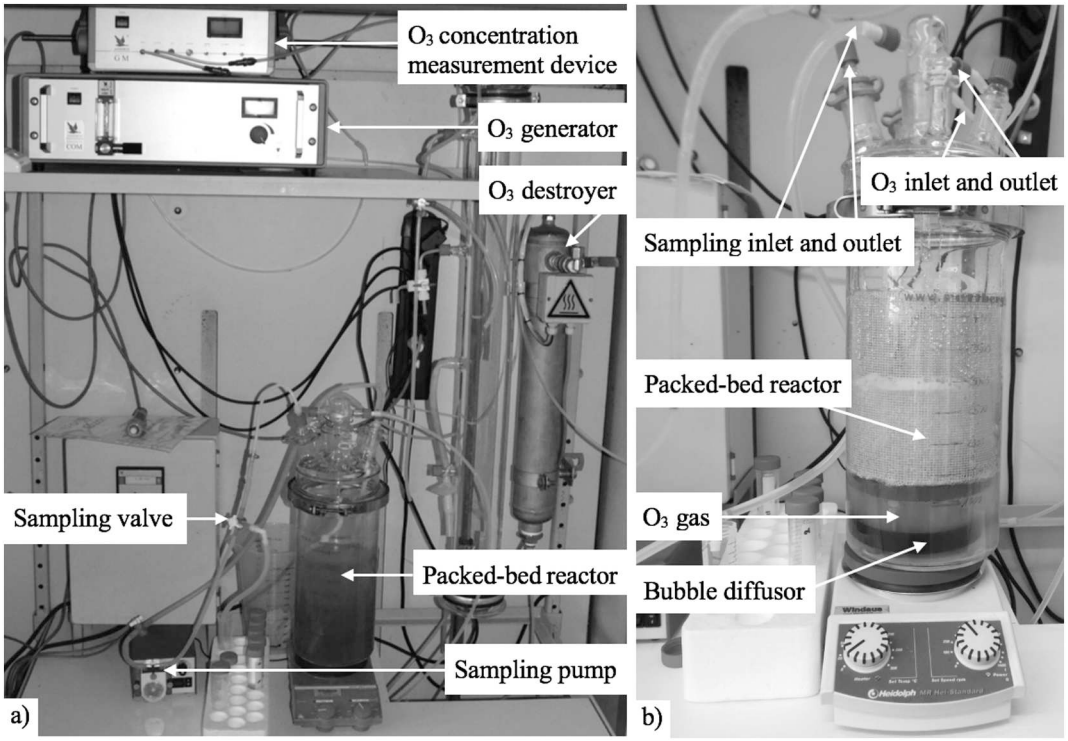

Fig. 2. (a) Experimental setup for ozonation and peroxone processes and (b) detailed view of the packed-bed reactor setup.

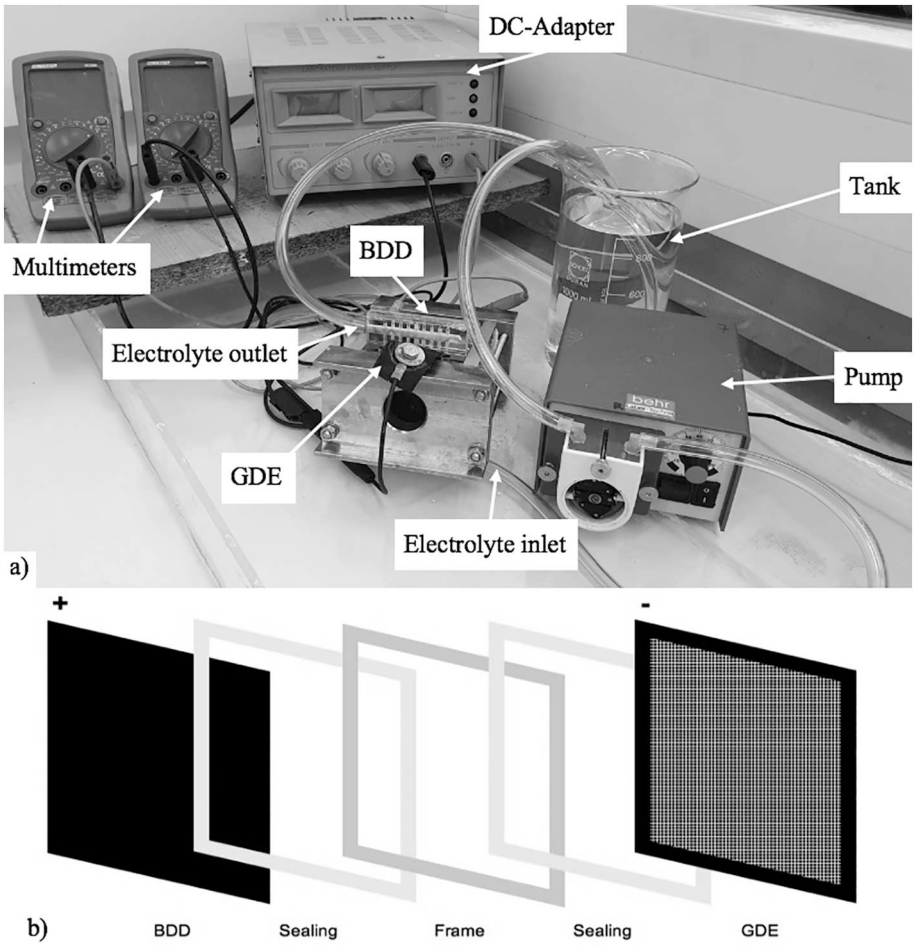

Fig. 3. (a) Photo and (b) schematic diagram of the experimental setup of the BDD/GDE reactor.

Table 2
Influence of ozone (and H_2O_2) input on COD removal after 4 h of ozonation.

Run	O_3 flow rate [mg/L]	$m_{O3,\ net}$ [mg]	COD_{Start} [mg/L]	COD_{End} [mg/L]	m_{COD} removal [mg]	O_3 demand [mgO_3/mg COD]	Reaction time [h]
1	81	5733	4668	3880	1576	3.6	4
2	66	4593	4671	4260	822	5.6	4
3	51	2580	4688	4392	592	4.4	4
4	31	580	4676	4524	304	1.9	4
5	81 + H_2O_2	5133	4790	3560	2460	2.1	4

is only approx. 2.6 times higher. A column in Table 2 displays the specific O_3 demand, i.e. the amount which was needed to remove 1 mg of COD. In contrast to the COD removal, the lowest specific O_3 demand was observed in the experiment with 31 mg/L O_3 (run 4), which leads to the proposition that a lower O_3 concentration results in a better specific COD removal. This was also supported by the preceding experiments, where a flow rate of 31 mg/L always resulted in the best specific O_3 demand. Despite the optimized O_3 generator, the mass transport seems to limit the degradation rate significantly.

It could have been shown that the specific O_3 demand could have been lowered to a value of 1.9 mg O_3 per mg m_{COD}. Of course, the specific demand depends on the composition of the COD, whether it is easily degradable or not. Sigge et al. found out that approx. 3.7 mg of O_3 is needed to break down 1 mg of m_{COD} in distillery WW [21], whereas Blonskaja et al. found out that 1.2 to 2.5 mg O_3/mg m_{COD} is needed for the treatment of WW from the yeast industry [22]. Hsu et al. found that 1.9 mg O_3/mg m_{COD} (at pH 7) is needed for the decolorization of Acid Blue 9, and 1.8 mg O_3/mg m_{COD} (at pH 7) for the ozonation of Direct Blue 71 [23].

In a fifth experiment (run 5), 2 mL H_2O_2 was added every 30 min for additional $^{\bullet}OH$ generation during another four-hour experiment using 81 mg/L O_3. This is a promising process for COD degradation [24]. As Table 2 shows, the COD of the artificial WW was reduced to a lower concentration with the additional H_2O_2 compared to the results obtained without H_2O_2. The degradation rate of the O_3 system could be increased further by feeding H_2O_2, showing a degradation rate of 51% within 4 h, but run 4 still showed the best yield through the lowest O_3 demand.

3.2. Electrochemical treatment

Table 3 shows the results obtained using the new electrochemical treatment. For comparative reasons the duration of the experiments was also 4 h.

To test the system under ambient conditions, run 6 was done without temperature control, the temperature increasing from approx. 22 to 46 °C. Two further experiments with temperature control (runs 7 and 8) were conducted at 40 and 25 °C, respectively. The experiment at 40 °C leads to an improvement in COD reduction, because cooler temperatures have a positive effect on the stability of H_2O_2, as already shown by Yazici et al. and Muddemann et al. [25,26]. They investigated the temperature-dependent stability of H_2O_2, and found a significant decomposition of H_2O_2 at 50 °C within 180 min, whereas it is almost stable at 20 °C.

Table 4
Comparison of specific power demands of ozonation, peroxone process and BDD/GDE.

	Ozonation	Ozonation	Peroxone	BDD/GDE
Run	1	4	5	8
COD degradation rate [g/m^3/h]	197.0	38.0	307.5	426.3
COD degradation [%]	17.0	3.3	25.7	38.1
Energy $demand_{O3}$ [kWh/kg COD]	125.4	48.0	46.3	
Energy $demand_{H2O2}$ [kWh/kg COD]			88.2[a]	
Energy $demand_{electrolysis}$ [kWh/kg COD]				93.6
Energy $demand_{total}$ [kWh/kg COD]	125.4	48.0	134.5	93.6

[a] Estimated with 15 kWh/kg H_2O_2.

As an overview, Table 4 shows a comparison of the specific energy demand for removing 1 kg of m_{COD}. The specific energy demands for each experiment were calculated on the basis of the energy demands of the devices. The consumption of the O_3 generator was measured as 22.2 kWh/kg O_3 (81 mg/L) and 25.8 kWh/kg O_3 (31 mg/L). For comparison, the energy demand to produce 1 kg O_3 ranges between 13 and 29 kWh/kg, according to Christensen et al. [27]. The measured values were calculated using the corresponding O_3 demands in mg O_3/mg m_{COD}. The value for the energy demand only considers the consumption of the O_3 generator, not any other devices. The average voltage (13.3 V) and current (3 A) were used to determine the specific energy demand of the BDD/GDE treatment. The energy demand for pumps etc. is also not taken into account.

It is clear that the lowest specific energy demand could be obtained by treating the WW with ozonation (run 4), followed by BDD/GDE (run 8), ozonation (run 1) and the peroxone process (run 5). The energy demand of the BDD/GDE treatment depends on the conductivity of the WW, the gap between the BDD and GDE and contact resistances. Comparing ozonation and electrochemical treatment (runs 1 and 8), it is apparent that both treatment steps achieve similar levels of COD reduction of approx. 1576 to 1705 mg/L. However, the BDD/GDE treatment leads to an energy saving of about 25% (125.4 compared with 93.6 kWh/kg m_{COD}). The highest energy consumption was found for the peroxone treatment. The reaction of O_3 and H_2O_2 is well-studied, as described by the work of Merényi et al. [20]. The dosage of H_2O_2 and O_3 can be adjusted to obtain a maximum $^{\bullet}OH$ yield, whereas work on optimizing the electrochemical WW treatment is still in progress [28,29]. It may be assumed that the energy demand could be further reduced by a WW treatment with an optimized cell design. This could lower the voltage between the electrodes to a minimum, leading

Table 3
Influence of temperature on COD removal after 4 h of BDD/GDE treatment.

Run	Temp. [°C]	Current [A]	Voltage, avg. [V]	COD_{Start} [mg/L]	COD_{End} [mg/L]	m_{COD} removal [mg]	Reaction time [h]
6	46[a]	3	11.8	4740	3329	1411	4
7	40	3	13.8	4550	3070	1480	4
8	25	3	13.3	4470	2765	1705	4

[a] No temperature control, maximum value at the end of the experiment.

to a significant decrease in energy costs.

4. Conclusion and outlook

A model WW close to the composition of solid-free WW from the vacuum toilets of trains was successfully treated in the electrochemical BDD/GDE reactor and compared with the results obtained using ozonation and peroxone processes. The COD removal during the electrochemical treatment was on the same level as that obtained by ozonation with 81 mg/L O_3, but the energy consumption was approx. 25% lower. The energy demand of the electrochemical reactor could be reduced still further by optimizing the reactor design or using a WW with higher conductivity. Both would lead to a lower cell voltage. For that reason, another possible application could be in treatment of WW with a high conductivity, maybe produced by an industrial process.

Additionally, further investigation of the removal of micropollutants will follow. It is important to determine the fate of persistent pharmaceuticals, especially for water destined for reuse. Electrochemical treatment with a combination of BDD and GDE seems to be a promising approach for the removal of chemicals which are normally resistant to degradation, due to the improved oxidation efficiency produced by combining $^{\bullet}OH$ and H_2O_2 generation. Furthermore, the disinfection and decoloration of WW is also possible with this EAOP concept [30–33], which may be an interesting option for the reuse of water in the vacuum toilets of trains.

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